QUARTZ: CRYSTAL GROWTH, CRYSTALLOGRAPHY, WAFER PRODUCTION

If, for certain applications, substrates are required which do not have the electrical properties of a semiconductor but rather a high optical transmission also in the ultraviolet and infra-red spectral range, high dielectric strength and high thermal conductivity, very high chemical stability or piezoelectric behaviour for, for example, oscillators, quartz wafers are usually the first choice.

This chapter describes the production of quartz wafers and attempts to illustrate the relatively complex crystal structure of quartz compared to silicon.

Manufacture of Quartz Crystals

The Raw Material

The raw materials for the culturing of quartz single crystals are naturally occurring, high-purity quartz crystals (so-called "lascas") which can be used in cm-sized fragments without any further purification stage for the crystal cultivation described in the following section.

Crystal Growth

Quartz monocrystals are formed via *hydrothermal synthesis* (Fig. 29).

Hereby, quartz crystallizes at a temperature of approx. 400°C and a pressure of 1000 - 1500 bar from a saturated NaOH solution at quartz seed crystals which have a slightly lower temperature than the crushed source quartz at the bottom of the container.

Quartz growth usually takes hours or days and forms monocrystals up to several kg weight. The quartz monocrystals formed hereby are cut into wafers and finally polished.

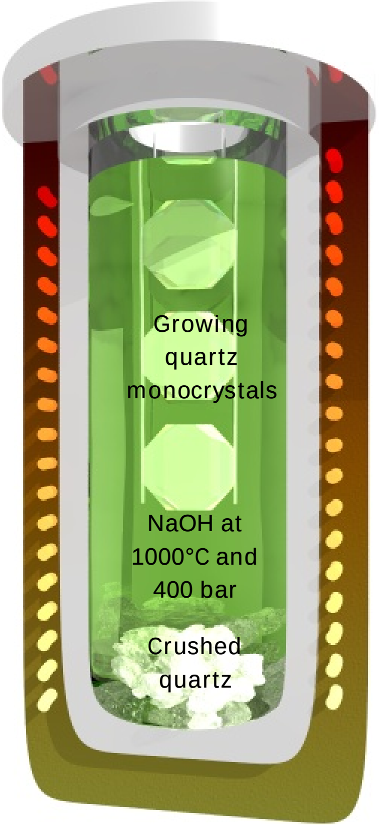


Fig. 29: Quartz monocrystals are formed via hydrothermal synthesis

Crystallography of Quartz

Thought Experiment: from Si to SiO_2

To obtain the chemical formula SiO_2 of quartz, as well as the basic bonding ratios in the quartz crystal, in a silicon monocrystal an oxygen atom imaginary is introduced from into each Si-Si bond (Fig. 30).

However, the result of this thinking experiment has little to do with the structure of a real quartz crystal where the angles and spatial orientations of Si-O-Si are very complex.

A Tetrahedron Trio as Basic Structure

In a quartz crystal, each silicon atom is surrounded tetrahedrally by

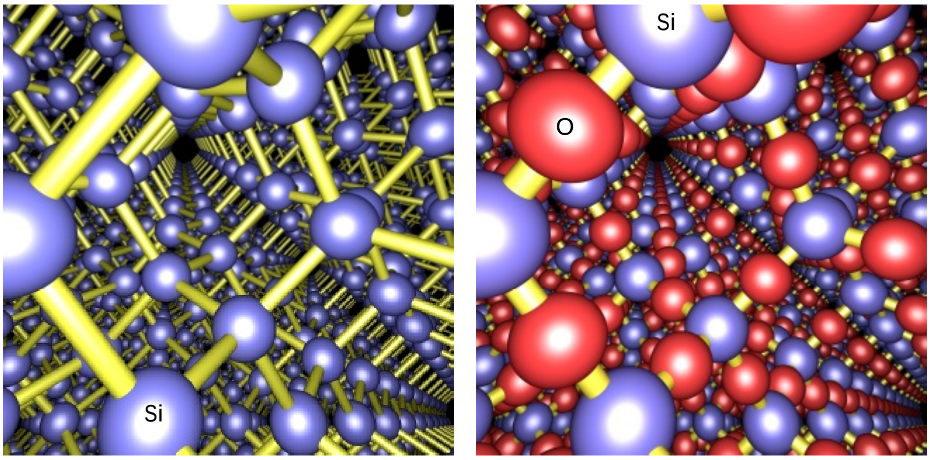


Fig. 30: If an oxygen atom (right, red balls) is added add to a silicon crystal (left) in each Si-Si bond, at least the basic bonding characteristics of a quartz crystal are attained: Silicon atoms surrounded tetrahedrally by four oxygen atoms. However, because the Si-O-Si bonds are not linear but bent in an actual quartz crystal, its structure is considerably more complex than shown here.

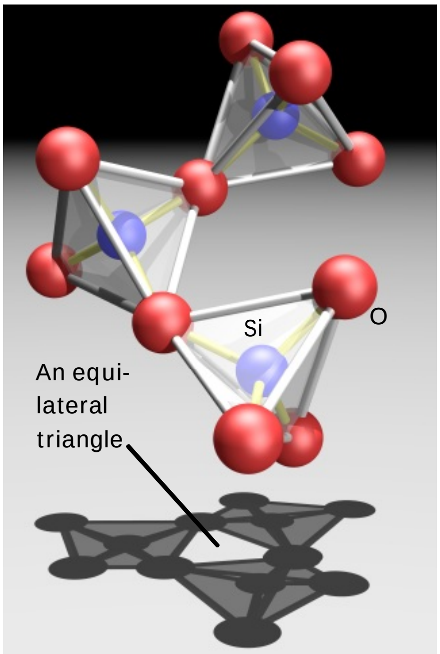
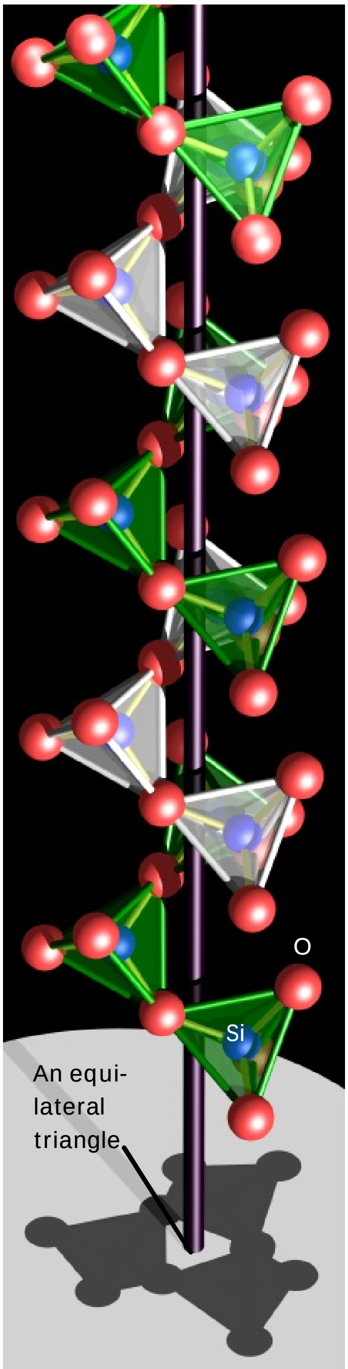


Fig. 31: (left) A basic structure of a quartz crystal consists of three Si-O-Si bonds linked tetrahedrally, each consisting of a central silicon atom and four O atoms bonded to it. Seen from a certain direction (here: from "above"), the three tetrahedrons form an equilateral triangle as a gap. Since this basic structure is not a unit cell, their chemical formula - Si_3O_{10} - is not consistent with that of quartz (SiO_2): In the following composition of these tetrahedral trios via Si-O + O-Si → Si-O-Si, O atoms are “split off virtually".

Fig. 32: (right) Congruently stacked tetrahedral trios (for improved clarity alternately coloured white and green) result in a helix, whose projection is perpendicular to its axis identical to that of a single tetrahedron trio.



four O atoms, where the shape of this tetrahedron differs slightly from a perfect tetrahedron due to the anisotropy of the quartz crystal. In each case two of these tetrahedra are linked over the tetrahedron corners via a Si-O-Si bond which is angled at 143.6°.

An ostensive, but not the smallest possible structure from which a quartz crystal can be constructed solely by translation (without additional rotation) in all three spatial directions is a “tetrahedral trio” (Fig. 31) formed from three such tetrahedra which reveal in a certain projection a threefold symmetry.

A Helix Consisting of Tetrahedral Trios

If several tetrahedron trios are stacked one on top of the other as shown in Fig. 32, the tetrahedra form a helix wound around an imaginary axis.

Since in this case the tetrahedron trios are not twisted against each other but are placed congruently on one another, the helix has the same threefold symmetry in a projection perpendicular to its axis as a single tetrahedron trio ("shadow-throw" in Fig. 31 and Fig. 32). Analogous to the thread of a screw, there is a dextrorotatory and a levorotatory variant for such a helix.

A Crystal of Helices

Several helices aligned parallel to one another and not mutually displaced in their longitudinal axis can now be linked to one another via O bonds as shown in Fig. 33.

The projection perpendicular to the axes of the helices reveals here equilateral triangular and significantly larger, scalene hexagonal channels which runs through the entire crystal in this direction (Fig. 33, right graphic).

Basic Structure vs. Unit Cell

The tetrahedral trio used as the basic structure is suitable for a spatially-visual representation of the structure of a quartz crystal as described in this section, but is hardly suitable for illustrating the orientation of the different crystal planes or the origin of the different facets of a real quartz crystal.

An extensive mathematical treatment via the so-called *unit cell* would be necessary, but we will do without it and take the mental leap for the representation of the crystal axes and planes of a quartz crystal.

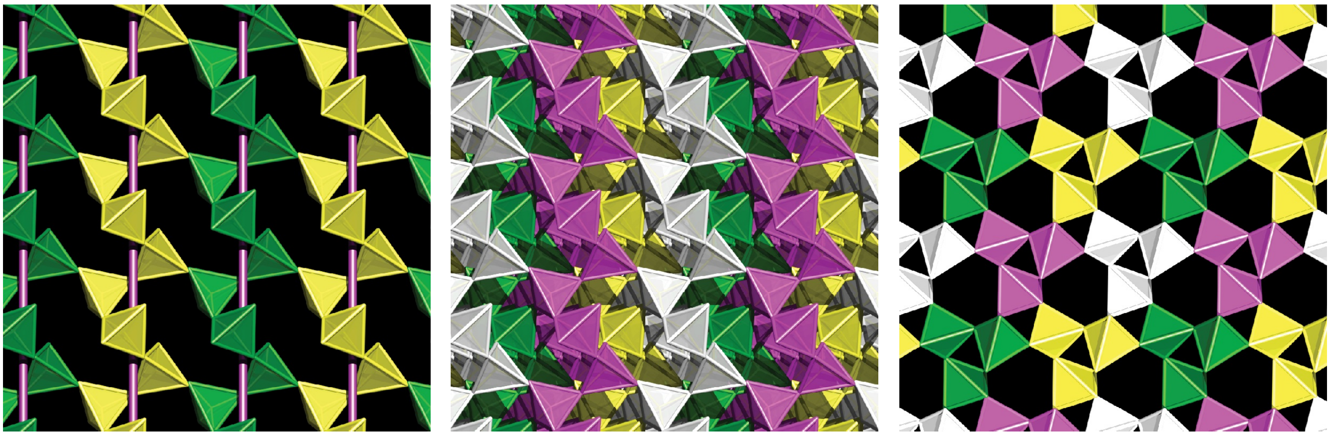


Fig. 33: The completed model of a quartz crystal is formed by a linkage of helices parallel over the corners (oxygen atoms) of the SiO_4 tetrahedra (left: first parallel to the image plane, centre: then perpendicular to it). A change to a viewing direction parallel to the helix axis (right) shows the symmetry of this arrangement. For clarity, each helix is shown consistently as a solid colour.

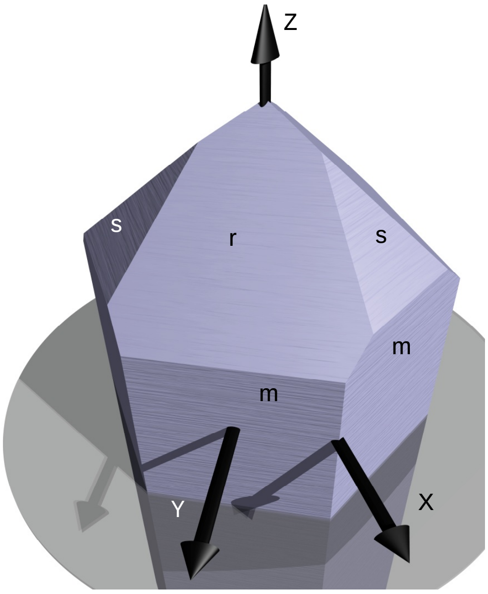


Fig. 35: The diagram of a quartz crystal with the crystal axes X, Y and Z, as well as certain crystal planes m, r and s

The Crystal Planes

Fig. 35 shows the idealized representation of a quartz crystal in its most common form, a hexagonal prism with two six-sided pyramids at both ends and with X, Y and Z designated crystal axes.

Like this idealized crystal, many real quartz crystals show three types of crystal faces: Six lateral faces (m) on the central six-sided prism, three larger triangular faces at the tips of the crystal (r) and three smaller, mostly triangular faces at the tips of the crystal (s).

Fig. 34 shows the regular arrangement of the silicon and oxygen atoms without representation of the tetrahedra in a viewing direction parallel to the crystal axes X, Y and Z as are relevant to the properties of the quartz wafer cut from the monocrystal.

Dextrorotatory and Levorotatory Quartz

The construction of a quartz crystal in this section was implemented arbitrarily from helices with a direction of rotation along the helix axis in the counter-clockwise direction. This results in the so-called *levorotatory* quartz, which also rotates the

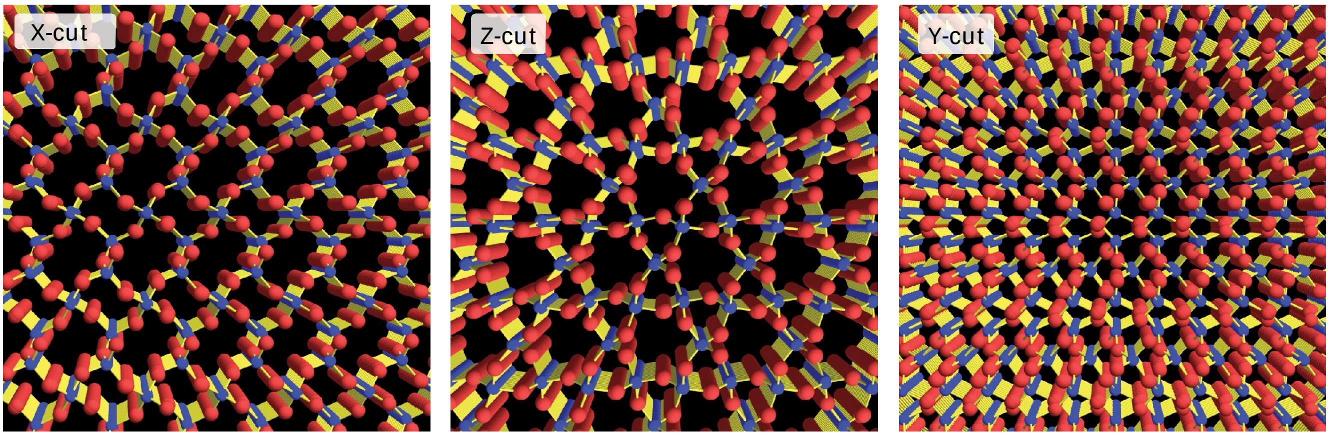


Fig. 34: A projection perpendicular to certain crystal planes reveals the symmetries of the bonding patterns of the silicon (blue) and oxygen (red) atoms for quartz cut perpendicular to the X axis (left), Z axis (centre), and Y axis.

polarization plane of incidental light parallel to the Z-axis (= parallel to the helix axes in Fig. 33) counter-clockwise.

Analogue to this, *dextrorotatory* quartz is constructed from helices, whose direction of rotation is clockwise along the axis, and which rotates the plane of polarized light clockwise.

According to this, quartz has a chirality (handedness). Dextrorotatory and levorotatory quartz cannot be converted into each other by rotation, but only via an (virtual) inversion.

In physical variables such as density, hardness, dielectric strength, optical absorption or thermal expansion coefficient which (in contrast to the circularly polarized light), the electric and the magnetic vector) have no chirality, the dextrorotatory and levorotatory quartz do not differ.

A-quartz and B-quartz

At room temperature, quartz exists as α-quartz as described in this chapter; at 573°C, the conversion to β-quartz is accompanied by a volume expansion of 0.45%.

In this inversion, the SiO_4 tetrahedra tilt in such a way that a six-fold symmetry follows from the threefold symmetry of α-quartz in the viewing direction of the helix axes (Z-axis, Fig. 33 right) without breaking or forming bonds. The hexagonal channels along the Z-axis now form equilateral hexagons with β-quartz.

Production of Quartz Wafers

The cutting of the wafer from the grown monocrystals with a wire or inside hole saw, the grinding and polishing is basically done with the same techniques as with silicon wafers.

Specifications of Quartz Wafers

Crystal Orientation

Quartz is a mono-crystalline material with various different crystal planes, each with its own periodic arrangement of silicon and oxygen atoms. Quartz wafers are usually cut from the mono-crystal parallel to these crystal planes and their orientation is correspondingly determined by "X-cut" (perpendicular to the X axis), "Y-cut" (perpendicular to the Y axis) or "Z-cut" (perpendicular to the Z axis) as shown in Fig. 35. In addition, there are still a lot of other orientations which are less clearly representable such as the "AT-cut" and "ST-cut" which correspond to the crystal planes tilted to the main crystal directions.

Since each crystal plane has its own bonding pattern on silicon and oxygen atoms, parameters such as thermal expansion coefficients, oscillation frequencies (quartz oscillators) or certain optical properties (rotation of the polarization plane of incident light along the Z axis) depend on the crystal orientation of the wafer.

Surfaces

Usually, quartz wafers are double-side polished, single-side polishing is available on request. The roughness of the polished side(s) is typically <1 nm, a value of < 0.5 nm which almost corresponds to atomic smoothness is also technically feasible.

Our Photoresists: Application Areas and Compatibilities

Recommended Applications[1]		Resist Family	Photoresists	Resist Film Thickness[2]	Recommended Developers[3]	Recommended Removers[4]
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ® 1500	AZ® 1505 AZ® 1512 HS AZ® 1514 H AZ® 1518	≈ 0.5 µm ≈ 1.0 - 1.5 µm ≈ 1.2 - 2.0 µm ≈ 1.5 - 2.5 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
		AZ® 4500	AZ® 4533 AZ® 4562	≈ 3 - 5 µm ≈ 5 - 10 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
		AZ® P4000	AZ® P4110 AZ® P4330 AZ® P4620 AZ® P4903	≈ 1 - 2 µm ≈ 3 - 5 µm ≈ 6 - 20 µm ≈ 10 - 30 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
		AZ® PL 177	AZ® PL 177	≈ 3 - 8 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Spray coating	AZ® 4999		≈ 1 - 15 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Dip coating	MC Dip Coating Resist		≈ 2 - 15 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® ECI 3000	AZ® ECI 3007 AZ® ECI 3012 AZ® ECI 3027	≈ 0.7 µm ≈ 1.0 - 1.5 µm ≈ 2 - 4 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
		AZ® 9200	AZ® 9245 AZ® 9260	≈ 3 - 6 µm ≈ 5 - 20 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	
	Elevated thermal softening point and high resolution for e. g. dry etching	AZ® 701 MiR	AZ® 701 MiR (14 cPs) AZ® 701 MiR (29 cPs)	≈ 0.8 µm ≈ 2 - 3 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
Positive (chem. amplified)	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® XT	AZ® 12 XT-20PL-05 AZ® 12 XT-20PL-10 AZ® 12 XT-20PL-20 AZ® 40 XT	≈ 3 - 5 µm ≈ 6 - 10 µm ≈ 10 - 30 µm ≈ 15 - 50 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
		AZ® IPS 6050		≈ 20 - 100 µm		
Image Reversal	Elevated thermal softening point and undercut for lift-off applications	AZ® 5200	AZ® 5209 AZ® 5214	≈ 1 µm ≈ 1 - 2 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF	TechniStrip® Micro D2 TechniStrip® P1316 TechniStrip® P1331
		TI	TI 35ESX TI xLift-X	≈ 3 - 4 µm ≈ 4 - 8 µm		
Negative (Cross-linking)	Negative resist sidewalls in combination with no thermal softening for lift-off application	AZ® nLOF 2000	AZ® nLOF 2020 AZ® nLOF 2035 AZ® nLOF 2070	≈ 1.5 - 3 µm ≈ 3 - 5 µm ≈ 6 - 15 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
		AZ® nLOF 5500	AZ® nLOF 5510	≈ 0.7 - 1.5 µm		
	Improved adhesion, steep resist sidewalls and high aspect ratios for e. g. dry etching or plating	AZ® nXT	AZ® 15 nXT (115 cPs) AZ® 15 nXT (450 cPs)	≈ 2 - 3 µm ≈ 5 - 20 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
			AZ® 125 nXT	≈ 20 - 100 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® P1316 TechniStrip® P1331 TechniStrip® NF52 TechniStrip® MLO 07

[1] In general, almost all resists can be used for almost any application. However, the special properties of each resist family makes them specially suited for certain fields of application.

[2] Resist film thickness achievable and processable with standard equipment under standard conditions. Some resists can be diluted for lower film thicknesses; with additional effort also thicker resist films can be achieved and processed.

[3] Metal ion free (MIF) developers are significantly more expensive, and reasonable if metal ion free development is required.

Our Developers: Application Areas and Compatibilities

Inorganic Developers

(typical demand under standard conditions approx. 20 L developer per L photoresist)

AZ® Developer is based on sodium phosphate and –metasilicate, is optimized for minimal aluminum attack and is typically used diluted 1 : 1 in DI water for high contrast or undiluted for high development rates. The dark erosion of this developer is slightly higher compared to other developers.

AZ® 351B is based on buffered NaOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated.

AZ® 400K is based on buffered KOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated.

AZ® 303 specifically for the AZ® 111 XFS photoresist based on KOH / NaOH is typically diluted 1 : 3 - 1 : 7 with water, depending on whether a high development rate, or a high contrast is required

Metal Ion Free (TMAH-based) Developers

(typical demand under standard conditions approx. 5 - 10 L developer concentrate per L photoresist)

AZ® 326 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water.

AZ® 726 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development)

AZ® 826 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development) and other additives for the removal of poorly soluble resist components (residues with specific resist families), however at the expense of a slightly higher dark erosion.

Our Removers: Application Areas and Compatibilities

AZ® 100 Remover is an amine solvent mixture and standard remover for AZ® and TI photoresists. To improve its performance, AZ® 100 remover can be heated to 60 - 80°C. Because the AZ® 100 Remover reacts highly alkaline with water, it is suitable for this with respect to sensitive substrate materials such as Cu, Al or ITO only if contamination with water can be ruled out..

TechniStrip® P1316 is a remover with very strong stripping power for Novolak-based resists (including all AZ® positive resists), epoxy-based coatings, polyimides and dry films. At typical application temperatures around 75°C, TechniStrip® P1316 may dissolve cross-linked resists without residue also, e.g. through dry etching or ion implantation. TechniStrip® P1316 can also be used in spraying processes. For alkaline sensitive materials, TechniStrip® P1331 would be an alternative to the P1316. Nicht kompatibel mit Au oder GaAs.

TechniStrip® P1331 can be an alternative for TechniStrip® P1316 in case of alkaline sensitive materials. TechniStrip® P1331 is not compatible with Au or GaAs.

TechniStrip® NI555 is a stripper with very strong dissolving power for Novolak-based negative resists such as the AZ® 15 nXT and AZ® nLOF 2000 series and very thick positive resists such as the AZ® 40 XT. TechniStrip® NI555 was developed not only to peel cross-linked resists, but also to dissolve them without residues. This prevents contamination of the basin and filter by resist particles and skins, as can occur with standard strippers. TechniStrip ® NI555 is not compatible with GaAs.

TechniClean™ CA25 is a semi-aqueous proprietary blend formulated to address post etch residue (PER) removal for all interconnect and technology nodes. Extremely efficient at quickly and selectively removing organo-metal oxides from Al, Cu, Ti, TiN, W and Ni.

TechniStrip™ NF52 is a highly effective remover for negative resists (liquid resists as well as dry films). The intrinsic nature of the additives and solvent make the blend totally compatible with metals used throughout the BEOL interconnects to WLP bumping applications.

TechniStrip™ Micro D2 is a versatile stripper dedicated to address resin lift-off and dissolution on negative and positive tone resist. The organic mixture blend has the particularity to offer high metal and material compatibility allowing to be used on all stacks and particularly on fragile III/V substrates for instance.

TechniStrip™ MLO 07 is a highly efficient positive and negative tone photoresist remover used for IR, III/V, MEMS, Photonic, TSV mask, solder bumping and hard disk stripping applications. Developed to address high dissolution performance and high material compatibility on Cu, Al, Sn/Ag, Alumina and common organic substrates.

Our Wafers and their Specifications

Silicon-, Quartz-, Fused Silica and Glass Wafers

Silicon wafers are either produced via the Czochralski- (CZ-) or Float zone- (FZ-) method. The more expensive FZ wafers are primarily reasonable if very high-ohmic wafers (> 100 Ohm cm) are required.

Quartz wafers are made of monocrystalline SiO_2, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO_2. The so-called JGS2 wafers have a high transmission in the range of ≈ 280 - 2000 nm wavelength, the more expensive JGS1 wafers at ≈ 220 - 1100 nm.

Our glass wafers, if not otherwise specified, are made of borosilicate glass.

Specifications

Common parameters for all wafers are diameter, thickness and surface (1- or 2-side polished). Fused silica wafers are made either of JGS1 or JGS2 material, for quartz wafers the crystal orientation needs to be defined. For silicon wafers, beside the crystal orientation (<100> or <111>) the doping (n- or p-type) as well as the resistivity (Ohm cm) are selection criteria.

Prime- ,Test-, and Dummy Wafers

Silicon wafers usually come as „Prime-grade“ or „Test-grade“, latter mainly have a slightly broader particle specification. „Dummy-Wafers“ neither fulfill Prime- nor Test-grade for different possible reasons (e. g. very broad or missing specification of one or several parameters, reclaim wafers, no particle specification) but might be a cheap alternative for e. g. resist coating tests or equipment start-up.

Our Silicon-, Quartz-, Fused Silica and Glass Wafers

Our frequently updated wafer stock list can be found here: è www.microchemicals.com/products/wafers/waferlist.html

Further Products from our Portfolio

Plating

Plating solutions for e. g. gold, copper, nickel, tin or palladium: è www.microchemicals.com/products/electroplating.html

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... è www.microchemicals.com/products/solvents.html

Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, … è www.microchemicals.com/products/etchants.html

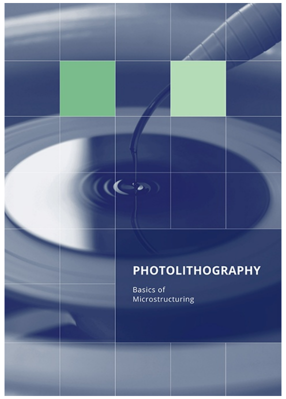
Etching Mixtures

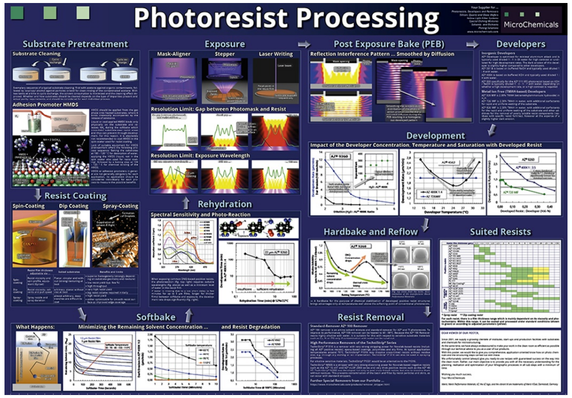
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

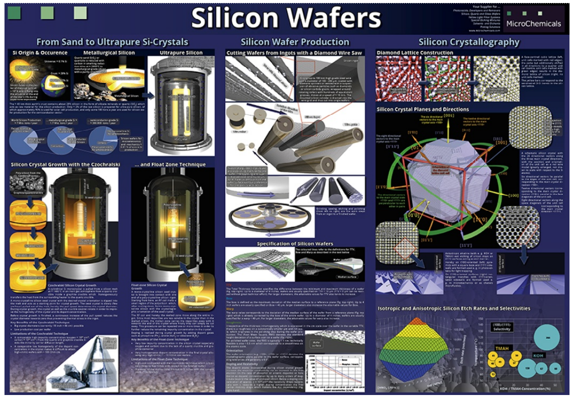
Further Information

Technical Data Sheets:	www.microchemicals.com/downloads/product_data_sheets/photoresists.html
Material Safety Data Sheets (MSDS):	www.microchemicals.com/downloads/safety_data_sheets/msds_links.html

Our Photolithography Book and -Posters







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